CC=Japan DATE=19920701 KIND=Kokai PN=04184861

METHOD FOR MANUFACTURING A LITHIUM BATTERY [Richiumu Denchi no Seizō Hōhō]

Masatake Nishio, Tomoya Murata, Keiji Fukuhara, and Hideaki Katsuno

UNITED STATES PATENT AND TRADEMARK OFFICE WASHINGTON, D.C. May 2009 TRANSLATED BY: SCHREIBER TRANSLATION, INC.

PUBLICATION COUNTRY	(10):	Japan
DOCUMENT NUMBER	(11):	04184861
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	19920701
APPLICATION NUMBER	(21):	02310266
APPLICATION DATE	(22):	19901116
INTERNATIONAL CLASSIFICATION	(51) :	H 01 M 2/36 10/40
PRIORITY COUNTRY	(33):	N/A
PRIORITY NUMBER	(31):	N/A
PRIORITY DATE	(32):	N/A
INVENTOR(S)	(72):	Masatake Nishio, Tomoya Murata, Keiji Fukuhara, and Hideaki Katsuno
APPLICANT(S)	(71):	Fuji Electrochemical Co., Ltd.
DESIGNATED CONTRACTING STATES	(81):	N/A
TITLE	(54):	METHOD FOR MANUFACTURING A LITHIUM BATTERY
FOREIGN TITLE	[54A]:	Richiumu Denchi no Seizō Hōhō

Specification

1. Title of the invention

Method for manufacturing a lithium battery

2. Patent Claims

- 1. A method for manufacturing a lithium battery characterized by the possession of a process whereby an electrode group provided by mutually segregating an anode and a cathode via a separator is housed within a cylindrical battery can, whereby, upon the dispensing of a non-aqueous electrolytic solution into the aforementioned battery can, a pressure-elevated state is achieved, and whereby normal pressure is then restored.
- 2. A method for manufacturing a lithium battery characterized by the possession of a process whereby an anode and a separator are stacked in proper order within a battery can, whereby, upon the dispensing of a non-aqueous electrolytic solution into the aforementioned battery can, a pressure-elevated state is achieved, and whereby normal pressure is then restored.
- 3. A manufacturing method mentioned in Claim 1 or 2 characterized by the fact that the aforementioned pressure-elevated state is a state where the pressure is at least $0.2 \, \mathrm{kg/cm^2}$ higher than normal pressure.

3. Detailed explanation of the invention

(Industrial application fields)

The present invention concerns a method for manufacturing a lithium battery.

(Prior art)

A spiral lithium battery may, for example, be provided by laminating, via a separator, a sheet-shaped anode inclusive, as an active material, of manganese dioxide, etc. and a sheet-shaped cathode inclusive, as an active material, of lithium, by housing, within a cylindrical battery can, an electrode group assembled by spirally coiling the obtained laminate, by dispensing a non-aqueous electrolytic solution into said can, and by sealing the opening of said battery can with a sealing component (e.g., terminal sheet, etc.).

The instance of a flat lithium battery, furthermore, generally uses a process whereby an anodic mixture compression-molded into a disc shape is mounted on the inner bottom plane of a short cylindrical battery can, whereby a separator made of a polypropylene non-woven fabric is mounted on the upper plane of said anodic mixture, whereby a specified volume of a non-aqueous electrolytic solution is dispensed via the upper portion of said separator, whereby a cathode is pressed onto said inner bottom plane, whereby a terminal sheet wherein the outer circumferential portion thereof is capped with an insulating sealing gasket is

mounted on the separator upper plane, and whereby a sealed battery is provided by pressing and clamping the sealing gasket in-between the opening of the battery can and the

<u>/2</u>

circumferential edge of said terminal sheet.

One obtained by solubilizing a solute (e.g., lithium perchlorate, etc.) into a non-aqueous organic solvent (e.g., propylene carbonate, dimethoxyethane, dioxolane, tetrahydrofuran, etc.) is used as said non-aqueous electrolytic solution.

Incidentally, the electrode group of the spiral lithium battery, for example, abides in a densely spirally coiled state, whereas since the non-aqueous electrolytic solution is viscous to a certain extent, it is difficult for the aforementioned dispensed non-aqueous electrolytic solution to osmotically seep through the interior of the electrode group. In the case of the flat non-aqueous electrolytic solution battery, furthermore, the anodic mixture placed on the battery can has been compression-molded at a rather high pressure, and therefore, the osmotic seepage of the nonaqueous electrolytic solution through the same is tenuous, as in the aforementioned case.

As far as lithium batteries of this type are concerned, therefore, it is necessary, for the purpose of inducing a sufficient absorption of the dispensed electrolytic solution into the anode, separator, etc., to execute an ageing treatment for a maximum of 30 min. or so after the dispensing of the electrolytic solution. Such an ageing treatment may, for example, be executed by configuring a zigzag portion within a manufacturing line and by securing a liquid absorption time within this zigzag portion.

(Problems to be solved by the invention)

In a case where the aforementioned ageing treatment is performed, however, a rather large space becomes necessary on a mass production line, and it becomes impossible to up the line rotation frequency since the liquid dispensing process serves as a limiting factor.

Moreover, even if the ageing time is invariable, for example, the liquid absorption rate varies depending on subtle differences of operative atmospheres and/or inter-lot variances of active materials and separators, and therefore, liquid absorption volumes of individual batteries mutually differ. In such a case, the electrolytic solution remaining unabsorbed upon the completion of ageing erupts out of the battery on a clamping and sealing occasion during a subsequent process, and therefore, the electrolytic solution volume must be designated at a minimal value ensuring a fail-proof absorption in the course of ageing. For this reason, it becomes impossible to dispense, into the battery, a necessary and sufficient volume of the electrolytic solution for inducing a discharge reaction, and therefore, it becomes difficult to up the discharge performances.

A method for executing this type of liquid dispensing operation within a reduced-pressure atmosphere may then seem feasible, although the boiling points of non-aqueous solvents used within the non-aqueous electrolytic solutions of lithium batteries of this type are often as low as 70 ~ 80°C. For this reason, in a case where the electrolytic solution is dispensed into a battery can within a reduced-pressure atmosphere, said electrolytic solution becomes evaporated in a boiled state, which is flawed in that the composition thereof varies, and thus, this method is unsuitable as a method for manufacturing a lithium battery.

The objective of the present invention, which has been conceived for the purpose of eradicating the foregoing problems, is to provide a method for manufacturing a lithium battery capable, since a necessary volume of an electrolytic solution can be absorbed, both assuredly and easily, within a battery, of minimizing the manufacturing space, of improving performances, and of stabilizing the quality.

(Mechanism for solving the problems)

The gist of the method of the present invention for manufacturing a lithium battery lies in the possession of a process whereby, upon the dispensing of a non-aqueous electrolytic solution into a battery can in which at least a partial power generation element(s) is being housed, whereby a pressure-elevated state is achieved, and whereby normal pressure is then restored.

In other words, in a case where said battery is a spiral or inside-out lithium battery, it suffices to execute the aforementioned sequence of liquid dispensing \rightarrow pressure elevation \rightarrow normal pressure restoration in a state where an electrode group provided by mutually segregating an anode and a cathode via a separator is being housed within a cylindrical battery can.

In a case where said battery is a flat (coin-shaped) lithium battery, furthermore, it suffices to execute a sequence of dispensing non-aqueous electrolytic solution into battery can \rightarrow pressure elevation \rightarrow normal pressure restoration in a state where an anode and a separator are being stacked in proper order within a battery can.

Such a process whereby a pressure-elevated state is achieved and whereby normal pressure is then restored may be executed as a singular process (cycle), or multiple (e.g., 2 ~ 3) cycles may instead be repeated.

There are no special restrictions on the pressure of the aforementioned pressure-elevated state, although it is desirable for the same to be at least 0.2 kg/cm² higher than normal pressure, more specifically, 0.2 ~ 4 kg/cm². In a case where said pressure is lower than 0.2 kg/cm², irregular effects become achieved, whereas in a case where the same is [higher than?] 4 kg/cm², a special pressure elevation apparatus equipped with a pressure-resistant structure becomes necessary, due to which cost appreciation becomes unavoidable, and furthermore, the fear of the eruption of the

non-aqueous electrolytic solution cannot be ruled out on an occasion where normal pressure is restored.

(Functions)

In a case where the pressure becomes elevated after an non-aqueous electrolytic solution has been dispensed into a battery can, air sealed and trapped in the battery interior (N_2 and/or Ar in cases where these gases are provided as manufacturing atmospheres) becomes compressed, and the non-aqueous electrolytic solution osmotically seeps deeply through the battery interior on this occasion. Even if normal pressure is subsequently restored, the osmotically seeped non-aqueous electrolytic solution remains as it is without retorting to the initial state thereof.

As a result, it becomes possible to induce, both smoothly and assuredly, the absorption of the electrolytic solution into the electrodes and/or separator.

(Application examples)

In the following, application examples will be explained.

Application Example 1

In Figures 1 and 2, an electrode group (4) was provided by laminating, via a separator (3) made of polypropylene, the respective sheets of an anode (1) inclusive, as an active

material, of manganese dioxide and a cathode (2) inclusive, as an active material, of metallic lithium or by spirally coiling the same together (A).

This electrode group (4) was inserted into a non-bottomless cylindrical battery can (5) provided by plating an iron base with Ni (B), and furthermore, a lead terminal (6) retrieved from the cathode (2) was spot-welded to the bottom plane of the battery can (C). (7) is a disc-shaped insulating sheet.

Next, 2 g of a non-aqueous electrolytic solution EL was dispensed into said battery can via an opening (D). Said non-aqueous electrolytic solution EL was obtained by solubilizing 1 mole/L of lithium trifluoromethanesulfonate (LiCF $_3$ SO $_3$) within a 1 : 1 : 1 (volume ratio) organic solvent mixture of propylene carbonate (boiling point = 241°C), dimethoxyethane (boiling point = 85°C), dioxolane (boiling point = 78°C), and ethylene carbonate (boiling point = 238°C).

A pressure-elevating treatment (E) was performed by placing the battery into which the aforementioned solution had been dispensed within an atmosphere bearing a pressure higher than normal pressure by $0.5~{\rm kg/cm^2}$ (e.g., placement within a pressurizing apparatus) for approximately 1 sec.

Subsequently, normal pressure was restored, and after a cathodic terminal unit wherein the respective outer circumferences of a terminal sheet (8) and a sealing sheet (9) were clamped by a sealing gasket (10) had been mounted on

the battery can opening, the battery can opening edge unit was clamped inward and sealed (F), as a result of which the cylindrical spiral lithium battery of Application Example 1 with a height of 33.5 mm and a diameter of 17 mm (B1) was prepared. (11) is a lead terminal mutually connecting the anode and sealing sheet (9).

A lithium battery morphologically and dimensionally identical to its counterpart of Application Example 1, on the other hand, was prepared according to procedures similar to the aforementioned ones except that a pressure higher than normal pressure by 0.1 kg/cm² was designated during a pressure-elevating treatment (Comparative Example Moreover, a lithium battery morphologically and dimensionally identical to its counterpart of Application Example 1 was procedures similar prepared according to the aforementioned ones except that an ageing treatment was performed at normal temperature over a 30-min. period in place of the pressure-elevating treatment (Prior Art Example 1).

10 each of the foregoing three types of batteries were prepared, and the eruption weights, after clamping and sealing, of the non-aqueous electrolytic solutions (mg) of the respective batteries were investigated. The obtained results are shown in Table I as the respective average values of 10 samples each.

Table I

	Eruption weight (mg)
Application Example 1	0
Comparative Example 1	15
Prior Art Example 1	122

Moreover, each of these three types of batteries was subjected, at an environmental temperature of 20°C, to intermittent discharge cycles (terminal volume: 2.6 V) of a 3-sec. discharge at a current of 900 mA followed by a 27-sec. discharge recess period. Table II shows the cycle numbers of the respective batteries as average values of five each. Moreover, the standard deviations of the cycle numbers of the respective batteries (cycle numbers) are also shown.

Table II

	Cycle number	Standard deviation
Application Example 1	1710	7.8
Comparative Example 1	1615	19.5
Prior Art Example 1	1520	30

Although the foregoing examples instantiate spiral batteries, it is obvious that the same principle is applicable to an inside-out lithium battery using a power generation element constituted by configuring, via a non-

/4

bottomless cylindrical separator on the outer circumference of a cathode comprising of a metallic lithium cylinder, a cylindrically molded anode and that excellent effects can likewise be obtained. In other words, it suffices, in this case, to orchestrate, after the aforementioned power generation element has been filled into a battery can, a sequence of dispensing of non-aqueous electrolytic solution \rightarrow pressure elevation \rightarrow normal pressure restoration.

Application Example 2

In Figures 3 and 4, a powdery mixture inclusive, as an active material, of manganese dioxide was pressed into a coin shape at a specified pressure (G), and the obtained anode (12) was pressed onto the inner bottom plane of a short cylindrical battery can (13) (H). In the figures, (14) is an anodic ring attached fixedly to the bottom plane of the battery can by means of welding, etc.

Atop the anode (12), furthermore, a separator (15) made of a polypropylene non-woven fabric was mounted (I), and furthermore, 0.25 g of an non-aqueous electrolytic solution EL bearing a composition identical to its counterpart of

Application Example 1 was dispensed via the upper plane of the separator (15) (D).

A pressure-elevating treatment was performed by placing this battery within an atmosphere bearing a pressure higher than normal pressure by $0.5~{\rm kg/cm^2}$ (e.g., placement within a pressuring apparatus) for approximately 1 sec., and subsequently, normal pressure was restored.

Next, a cathodic terminal unit constituted by a cathode (16) comprising of metallic lithium, a sealing gasket (17) made of a cyclic synthetic resin, and a terminal sheet (18) wherein the cathode (16) was pressed onto the inner bottom plane thereof and wherein the outer circumference thereof was clamped with the sealing gasket (17) was mounted on the opening of the battery can (H). Moreover, the opening edge of the battery can was clamped inward for sealing the battery can (F), as a result of which the flat lithium battery of Application Example 2 with a height of 3.2 mm and a diameter of 20 mm (B2) was prepared.

A morphologically and dimensionally identical lithium battery, on the other hand, was prepared according to similar procedures except that a pressure higher than normal pressure by 0.1 kg/cm² was designated during a pressure-elevating treatment (Comparative Example 2). Moreover, a morphologically and dimensionally identical lithium battery was prepared according to similar procedures except that an ageing treatment was performed at normal temperature over a

30-min. period in place of the pressure-elevating treatment (Prior Art Example 2).

10 each of the foregoing three types of batteries were prepared, and the eruption weights, after clamping and sealing, of the non-aqueous electrolytic solutions (mg) of the respective batteries were investigated. The obtained results are shown in Table I [sic: Presumably "III"] as the respective average values of 10 samples each.

Table III

	Eruption weight (mg)
Application Example 2	3
Comparative Example 2	6
Prior Art Example 2	58

Moreover, these batteries were discharged at an environmental temperature of 20°C, at a constant resistance of 15 k Ω , and at a terminal voltage of 2.5 V, and the discharge times (hours) of the respective batteries on this occasion were investigated. Table II [sic: Presumably "IV"] shows the obtained results as average values of five each. Moreover, the standard deviations of the discharge times (hours) of the respective batteries are also shown.

Table IV

	Discharge time	Standard deviation
Application Example 2	1110	12
Comparative Example 2	1020	16
Prior Art Example 2	990	29

(Effects of the invention)

As has been mentioned above, since ageing is unnecessary for the method of the present invention for manufacturing a lithium battery, a small manufacturing space suffices. Moreover, since a necessary volume of a non-aqueous electrolytic solution can be dispensed, goals of improving the performances of the battery and of stabilizing the quality of the same can be realized.

4. Brief explanation of the figures

Figure 1 is a demonstrational diagram provided for explaining the manufacturing process of Application Example 1 of the present invention, whereas Figure 2 is a diagram which shows a cross-sectional view of the battery of Application Example 1, whereas Figure 3 is a demonstrational diagram provided for explaining the manufacturing process of Application Example 2, whereas Figure 4 is a diagram which

shows a cross-sectional view of the battery of Application Example 2.

(1) and (12): Anodes; (2) and (16): Cathodes; (3) and (15): Separators; (5) and (13): Battery cans; (8) and (18): Terminal sheets; (10): Insulating gasket.

Patent Applicant: Fuji Electrochemical Co., Ltd.

Agent: Yukio Omata

/<u>5</u>

Figure 1







